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(54) **Heterogeneous gas generant charges**

(57) A gas generant charge comprises a heterogeneous mixture of a first gas generant composition hav-

ing a first pyrotechnic profile and a first effluent profile and a second gas generant charge having a second pyrotechnic profile and a second effluent profile.

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Description

The present invention is directed to gas generant compositions for inflating automotive airbags and other devices in which rapid production of high volumes of gas is required. More particularly, the invention is directed to a gas generant charge which is a heterogeneous mixture of two types of gas generant compositions. The gas generant compositions of the heterogeneous mixture complement each other, producing combustion products which are both low in undesirable gases and low in particulate matter.

Most automotive air bag restraint systems, presently in use, use gas generant compositions in which sodium azide is the principal fuel. Because of disadvantages with sodium azide, particularly instability in the presence of metallic impurities and toxicity, which presents a disposal problem for unfired gas generators, there is a desire to develop non-azide gas generant systems, and a number of non-azide formulations have been proposed. However, to date, non-azide gas generants have not made significant commercial inroads.

Alternatives to azides which have been proposed, e.g., in U.S. Patent No. 5,035,757, the teachings of which are incorporated herein by reference, include azole compounds, including tetrazole and triazole compounds. Tetrazole compounds include 5-amino tetrazole (AT), tetrazole, bitetrazole and metal salts of these compounds. Triazole compounds include 1,2,4-triazole-5-one, 3-nitro 1,2,4-triazole-5-one and metal salts of these compounds. Although all of the above azole compounds are useful fuels in accordance with the present invention, AT is the most commercially important of these.

Gas generant systems include, in addition to the fuel component, an oxidizer. Proposed oxidizers for use in conjunction with azole fuels include alkali and alkaline earth metal salts of nitrates, chlorates and perchlorates.

Several gas generant processing procedures utilize water. Water-processing reduces hazards of processing gas generant materials. It is therefore desirable that gas generant compositions be formulated so as to facilitate water processing. One example of water processing, taught, e.g., in U.S. Patent No. 5,015,309, the teachings of which are incorporated by reference, involves the steps of

1. Forming a slurry of the generant ingredients with water.
2. Spray drying the slurry to form spherical prills of diameter 100-300 microns.
3. Feeding the prills via gravity flow to a high speed rotary press.

In order to properly feed the tablet press, one needs well formed spherical prills. Without prills, plugging or bridging in the feed system is a common occurrence. Without prills, it is difficult to achieve uniform, high speed filling of the tablet press. These prills will not form in the spray drying step without at least a portion of the generant being water soluble. Typical slurries contain up to 35% water and it is preferred that at least 15% of the solid ingredients need to be soluble in the slurry.

Another common production technique, (e.g. U.S. Patent 5,084,218), the teachings of which are incorporated herein by reference, involves the following steps:

1. Forming a slurry of the generant ingredients with water.
2. Extruding the slurry to form spaghetti like strands.
3. Chopping and spheronizing the strands into prills.
4. Tableting of the prills as described previously.

The chopping and spheronizing step to form prills will not be successful unless a portion of the generant is water soluble.

A problem encountered with gas generant compositions which utilize tetrazoles or triazoles as fuel is the production of undesirable gases, such as CO, NO_x, NH₃, and HCN. U.S. Patent No. 5,467,715 to Robert Taylor et al, the teachings of which are incorporated herein by reference, describes a gas generant composition which uses as fuel, in addition to a tetrazole or triazole, a water-soluble fuel, such as guanidine nitrate, and as the oxidizer, a transition metal oxide, plus, preferably, an additional oxidizer, such as strontium nitrate. This composition is aqueous-processable, and also minimizes levels of undesirable combustion gases. Nevertheless, the automotive industry is becoming increasingly sensitive to undesirable combustion gases and is imposing increasingly stricter standards. Thus, there is a continuing need to provide gas generant formulations producing further reduced levels of undesirable gases.

As described in U.S. Patent No. 5,431,103, the teachings of which are incorporated herein by reference, the gas generant composition described in above-referenced U.S. Patent No. 5,476,715 are auto-ignitable, auto-igniting, e.g.,

in the event of a vehicle fire, at a temperature substantially below temperatures where ignitor housings, particularly aluminum ignitor housings, weaken.

U.S. Patent No. 3,785,149 issued 15 January 1974 to Timmerman, the teachings of which are incorporated herein by reference, describes gas generant compositions which produce combustion gases which are substantially entirely carbon dioxide and water. The gas generant compositions of U.S. Patent No. 3,785,149 use as the fuel an organic compound which contains only the elements carbon, hydrogen and oxygen, the organic compound being a compound containing carboxylic acid groups or carboxylic acid salt groups and therefore being high in oxygen content. The oxidizer is an alkali metal, preferably sodium or potassium, chlorate or perchlorate. One problem with this type of fuel is that it produces high levels of particulate material which appear as smoke in the interior of a vehicle when the airbag deploys. While such "smoke" may not be particularly harmful, it may cause an occupant of a vehicle or a rescuer to incorrectly believe that the vehicle is on fire. Another problem is poor compatibility with inflators formed of aluminum or containing aluminum parts. The high combustion temperatures of these gas generant compositions tends to destroy aluminum parts, e.g., burn holes through the inflator housing or filter pack.

Thus, it can be seen that different gas generant compositions may produce different types of undesirable effluents, either gases or particulates. Often, it is difficult to reduce one or more specific undesirable effluent below a predetermined standard.

Here, it should be borne in mind that it is not necessary to reduce every undesirable effluent in gas generant compositions to zero. Exposure of a vehicle's occupant to gas generant effluent is very brief, and it is only necessary to ensure that the occupant is not subject to significant risk of harm by gas generant effluent during that very brief exposure. Also, the total amount of undesirable effluent of gas generants has extremely little effect on the general environment.

Formulating a gas generant composition for any particular application requires balancing of a number of pyrotechnic parameters, such as burn rate, combustion temperature, gas volume per weight of generant composition, etc. In addition, production of undesirable effluents, including both gases and particulates, must be considered.

As pyrotechnic and effluent characteristics are known for a wide variety of gas generant compositions, it might seem logical to mix the ingredients of several known compositions together and thereby balance the various pyrotechnic and effluent characteristics of different compositions. For example, in compositions which contain the elements C, H, O, N, and one or more metals, it is typically difficult to control levels of NO_x and NH_3 (CO may also be a problem, but may be controlled by formulating to burn at sufficiently low temperatures where CO production is minimized). On the other hand, in compositions which contain the elements C, H, O and one or more metals, CO levels are often problematic. It would seem logical, therefore, to mix the components of a gas generant composition in which NO_x and NH_3 levels are problematic and a generant composition in which CO levels are problematic to provide a gas generant composition in which levels of all undesirable gases are at sufficiently low levels.

However, this approach does not work when compositions are produced by common methods in which the components of the gas generant compositions are generally homogeneously mixed. When the components of two or more significantly different gas generant compositions are mixed together, the pyrotechnic and effluent characteristics tend not to be a weighted average of the two compositions. Instead, the pyrotechnic and effluent profiles of such mixed compositions tend to be unpredictable. This is because, upon combustion, chemical reactions invariably occur between the components selected according to the individual known compositions. Also, when homogeneously mixing components of two different gas generant compositions, there may be chemical interactions during the period prior to deployment. Even the possibility of such storage interactions may cause an airbag manufacturer to reject a mixed composition which has not been adequately tested for storage stability.

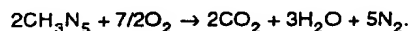
In accordance with the present invention, there is provided a heterogeneous mixture between a first separately compounded gas generant composition and at least a second separately compounded gas generant composition, whereby the pyrotechnic and gas effluent profiles of the heterogeneous gas generant composition resembles a weighted average of the gas generant compositions. By production of a heterogeneous, rather than a homogeneous mixture, cross-chemical reactions are avoided both prior to deployment and during gas generant combustion.

According to a specific aspect of the invention, a gas generant charge which provides low levels of undesirable gases and low levels of particulate matter upon combustion is a heterogeneous mixture of two gas generant compositions, the mixture comprising between about 80 and about 95 wt% of a first gas generant composition 1) and between about 5 and about 20 wt% of a second gas generant composition 2). The first gas generant composition 1) comprises between about 20 and about 40 wt% of fuel A) and between about 60 and about 80 wt% of oxidizer B). Between about 50 and about 85 wt% of the fuel A) is a triazole or tetrazole A'), between about 15 and about 50 wt% of the fuel is a watersoluble fuel A'') such as guanidine nitrate, ethylene diamine dinitrate or similar compounds. At least about 20 wt% of the oxidizer B) up to 100%, preferably at least about 50 wt%, comprises a transition metal oxide B'); balance of the oxidizer B'') alkali and/or alkaline earth metal nitrates, chlorates or perchlorates. The use of transition metal oxides as a major oxidizer component results in lower combustion temperatures, resulting in lower production of toxic oxides. The second gas generant composition 2) comprises between about 30 and about 65 wt% of a fuel C) which is

an organic compound containing only the elements carbon, hydrogen, and oxygen, the oxygen content being between about 35 and about 65 wt% of the organic compound, and between about 35 and about 70 wt% of an oxidizer D) which is an alkali metal chlorate or perchlorate.

Herein, unless otherwise stated, all percentages are by weight. The weight percentage of each gas generant composition and its components are calculated relative to the active ingredients, i.e., the total of fuel and oxidizer components. The weight percentages of other ingredients, such as coolants, fillers, pressing aids, etc., are calculated relative to the total active ingredients of each gas generant composition, the total of oxidizer plus fuel being 100%.

While the major fuel component A¹) of the first gas generant composition 1) may be selected from any of the tetrazole and triazole compounds listed above and mixtures thereof; from an availability and cost standpoint, 5-aminotetrazole (AT) is presently the azole compound of choice. The purpose of the fuel is to produce carbon dioxide, water and nitrogen gases when burned with an appropriate oxidizer or oxidizer combination. The gases so produced are used to inflate an automobile gas bag or other such device. By way of example, AT is combusted to produce carbon dioxide, water and nitrogen according to the following equation:



To facilitate processing in conjunction with water, a minor portion of the first 1) fuel, i.e., between about 15 and about 50 wt% of the fuel, is a water soluble fuel A²). While water-soluble oxidizers, such as strontium nitrate also facilitate water-processing, over-reliance on such water-soluble oxidizers tend to produce undesirably high combustion temperatures. Specific desirable characteristics of water-soluble fuels are:

The compound should be readily soluble in water, i.e., at least about 30 gm/100 ml. H₂O at 25°C;

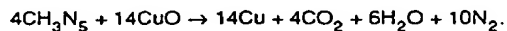
The compound should contain only elements selected from H, C, O and N;

When formulated with an oxidizer to stoichiometrically yield carbon dioxide, nitrogen, and water, the gas yield should be greater than about 1.8 moles of gas per 100 grams of formulation; and

When formulated with an oxidizer to stoichiometrically yield carbon dioxide, water and nitrogen, the theoretical combustion temperature at 1000 psi should be low, preferably, less than about 1800°K.

Compounds that most ideally fit the above criteria are nitrate salts of amines or substituted amines. Suitable compounds include, but are not limited to, the group consisting of guanidine nitrate, aminoguanidine nitrate, diaminoguanidine nitrate, semicarbazide nitrate, triaminoguanidine nitrate, ethylenediamine dinitrate, hexamethylene tetramine dinitrate, and mixtures of such compounds. Guanidine nitrate is the currently preferred water-soluble fuel.

Generally any transition metal oxide will serve as an oxidizer B¹). Particularly suitable transition metal oxides include ferric oxide and cupric oxide. The preferred transition metal oxide is cupric oxide which, upon combustion of the gas generant, produces copper metal as a slag component. The purpose of the oxidizer is to provide the oxygen necessary to oxidize the fuel; for example, CuO oxidizes AT according to the following equation:



The transition metal oxide B¹) may comprise the sole oxidizer in the first fuel or it may be used in conjunction with other oxidizers B²) including alkali and alkaline earth metal nitrates, chlorates and perchlorates and mixtures of such oxidizers. Of these, nitrates (alkali and/or alkaline earth metal salts) are preferred, and strontium nitrate is currently most preferred. Nitrate oxidizers increase gas output slightly. Alkali metal nitrates are particularly useful as ignition promoting additives.

The first gas generant composition 1) may optionally contain a catalyst up to about 3 wt%, typically between about 1 and about 2 wt%. Boron hydrides and iron ferricyanide are such combustion catalysts. Certain transition metal oxides, such as copper chromate, chromium oxide and manganese oxide, in addition to the oxidizer function, further act to catalyze combustion.

To further reduce reaction temperature, coolants may also optionally be included in the first gas generant composition at up to about 10 wt%, typically between about 1 and about 5 wt%. Suitable coolants include graphite, alumina, silica, metal carbonate salts, transition metals and mixtures thereof. The coolants may be in particulate form, although if available, fiber form is preferred, e.g., graphite, alumina and alumina/silica fibers.

Suitable fuels C) for the second gas generant composition 2) include, but are not limited to oxalic acid, malonic acid, succinic acid, tartaric acid, mucic acid, citric acid, salts thereof and mixtures thereof. A currently preferred fuel is tartaric acid. Fuel compounds containing carboxylic acids are reactive with transition metal oxides; thus, the components of the first gas generant composition and second gas generant composition cannot be compounded together.

Accordingly, the gas generant charges of the present invention must be heterogeneous.

The oxidizer D) for the second gas generant composition 2) is an alkali metal chlorate or perchlorate, particularly sodium chlorate, potassium chlorate, sodium perchlorate and potassium perchlorate.

As with the first gas generant composition, other ingredients known in the art, such as slag formers, processing aids, and/or burn rate catalysts may be optional or desirable in the second gas generant composition.

The first and second gas generant compositions are mutually beneficial when provided in a gas generant charge. The second gas generant composition reduces undesirable gases produced by the first gas generant composition. The first gas generant composition minimizes particulate matter produced by the second gas generant composition.

A heterogeneous charge may be provided in several manners. Powders of the two composition may be separately pressed into tablets or wafers and loaded into the inflator as two separate tablets or wafers. A "two headed" tablet can be manufactured of the two gas generant compositions by partial compaction of powders of one of the compositions, addition of powder of the second composition and final compaction for loading into the inflator as tablet or wafers. The currently preferred method is to dry blend powders of the two composition and press the dry-blended mixture into tablets or wafers. For producing tablets or wafers by any of the above methods, particularly the dryblend method, it is preferred that the gas generant composition powders have particle sizes between about 25 and about 250 microns.

It is generally desirable to pelletize the gas generant composition. If so, up to about 1 wt%, typically 0.2-0.5 wt% of a pressing aid or binder may be employed. If the two generants are separately pelletized or tableted, binders or pressing aids will be added to each gas generant composition. If powders of the two generant compositions are pelletized or tableted together, the binder or pressing aid will be added to a mixture of powders of the two gas generant compositions. The binders or pressing agents may be selected from materials known to be useful for this purpose, including molybdenum disulfide, polycarbonate, graphite, Viton®, nitrocellulose, polysaccharides, polyvinylpyrrolidone, sodium silicate, calcium stearate, magnesium stearate, zinc stearate, talc, mica minerals, bentonite, montmorillonite and others known to those skilled in the art. A preferred pressing aid/binder is molybdenum disulfide. If molybdenum disulfide is used, it is preferred that an alkali metal nitrate be included as a portion of the oxidizer. Alkali metal nitrate in the presence of molybdenum disulfide results in the formation of alkali metal sulfate, rather than toxic sulfur species. Accordingly, if molybdenum disulfide is used, alkali metal nitrate is used as a portion of the oxidizer in an amount sufficient to convert substantially all of the sulfur component of the molybdenum disulfide to alkali metal sulfate. This amount is at least the stoichiometric equivalent of the molybdenum disulfide, but is typically several times the stoichiometric equivalent. On a weight basis, an alkali metal nitrate is typically used at between about 3 and about 5 times the weight of molybdenum disulfide used.

The invention will now be described in greater detail by way of specific examples.

Comparative Examples 1 and 2; Examples 3 and 4

A first gas generant composition is formulated as follows: 69.55 wt% cupric oxide, 19.45 wt% 5-aminotetrazole, 6 wt% guanidine nitrate, and 5 wt% strontium nitrate. A second gas generant composition is formulated with 59.08 wt% potassium perchlorate and 40.92 wt% tartaric acid. Each of these compositions was manufactured by charging a vessel with water sufficient to yield a 30 wt% slurry, adding the solid ingredients, and mixing with a high shear mixture. Each slurry was poured into a tray and dried in an oven at 85-105°C until the material was dry enough to be pressed through a 6 mesh screen. Drying was then completed.

The materials were each tableted on a high speed rotary tablet press, tablets being formed 0.25" in diameter, 0.07" thick.

Comparative Example 1 was the first gas generant composition alone. Comparative Example 2 is the second gas generant composition alone. Example 3 was a mixture 28 wt% of tablets of the first gas generant composition and 12 wt% of the second gas generant composition. Example 4 was tablets of a dryblended mixture of the first and second gas generant compositions in the same weight percentages as Example 3.

Inflator tests using a 55 gram load exhausted into a 100 cubic foot tank are shown in the table below. Gas levels are given in parts per million by volume (ppm); particulate matter is expressed in grams.

	Comparative Example 1	Comparative Example 2**	Example 3	Example 4
NO _x	60-100	N/A	30-40	10-20
Ammonia	200-200	N/A	1-5	1-5

**In Comparative Example 2, only 25 grams of generant is used because higher loads result in excessively high pressures; particulate levels are calculated relative to a 55 gram charge.

(continued)

	Comparative Example 1	Comparative Example 2**	Example 3	Example 4
HCN	5-10	N/A	1-5	1-5
Particulate	<0.5	>2.0	<0.5	<0.5
I.C.*	good	poor to unacceptable	fair	fair

*Inflator compatibility

**In Comparative Example 2, only 25 grams of generant is used because higher loads result in excessively high pressures; particulate levels are calculated relative to a 55 gram charge.

It is seen that a mixture of the first and second gas generant compositions in Examples 3 and 4 produce significantly less undesirable gas than does the first gas generant composition (Comparative Example 1) alone, and less particulate matter than the second gas generant (Comparative Example 2) alone.

While the invention has been exemplified herein with reference to mixtures of certain specific gas generant compositions, the invention applies generally to heterogeneous mixing of a first and at least a second gas generant compositions. When heterogeneously mixed, the pyrotechnic and effluent characteristics, including gas effluent and particulate effluent, tends to be a weighted average of the heterogeneously mixed gas generant compositions. Although the invention has been exemplified with respect to heterogenous mixtures of two gas generant compositions, heterogeneous mixing should apply as well to mixtures of three or more gas generant compositions.

The invention provides for relative predictability of pyrotechnic and effluent profiles when using two or more gas generant compositions. As airbag applications become more specific, e.g., driver-side, passenger-side, side-impact, and with specifics for particular vehicles, there is a need to be able to customize pyrotechnic and gas effluent profiles. The invention provides the ability to so customize pyrotechnic and effluent characteristics with substantial predictability and confidence.

Claims

1. A gas generant charge comprising a heterogeneous mixture of between 50 and 95 wt% of a first gas generant composition (1) and between 5 and 20 wt% of a second gas generant composition (2), based on the total weight of (1) plus (2),

said first gas generant composition (1) comprising between 20 and 40 wt% of fuel (A) and between 60 and 80 wt% of oxidizer (B),
between 50 and 85 wt% of said fuel (A) being a triazole or tetrazole compound (A¹), between 15 and 50 wt% of said fuel being a water-soluble fuel (A²)

at least 20 wt% of said oxidizer (B), up to 100%, being a transition metal oxide (B¹); balance of said oxidizer being selected from a group (B²) consisting of alkali and/or alkaline earth metal nitrates, chlorates or perchlorates,

said second gas generant composition (2) comprising between 30 and 65 wt% of a fuel (C) which is an organic compound containing only the elements carbon, hydrogen, and oxygen, the oxygen content being between 35 and 65 wt% of said organic compound, and between about 35 and 70 wt% of an oxidizer (D) which is selected from alkali metal chlorates, alkali metal perchlorates, and mixtures thereof.

2. A gas generant charge in accordance with Claim 1 wherein said transition metal oxide is CuO.

3. A gas generant charge in accordance with Claim 1 or claim 2, wherein said water soluble fuel (A²) is selected from guanidine nitrate, aminoguanidine nitrate, diaminoguanidine nitrate, semicarbazide nitrate, triaminoguanidine nitrate, ethylenediamine dinitrate, hexamethylene tetramine dinitrate, and mixtures thereof.

4. A gas generant charge in accordance with claim 3 wherein said water-soluble fuel (A²) is guanidine nitrate.

5. A gas generant charge in accordance with any preceding Claim wherein said first and second gas generant compositions are pelletized in separate tablets or wafers.

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6. A gas generant charge in accordance with any one of Claims 1 to 4 wherein said first and second gas generant composition are copelletized from a dryblend mixture of said gas generant compositions.
7. A gas generant charge in accordance with any preceding Claim wherein said fuel (C) of said second gas generant composition (2) is tartaric acid.
8. A gas generant charge in accordance with any preceding claim wherein said oxidise (D) of the second gas generant charge (2) is potassium perchlorate.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 7233

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 150 431 A (WNC NITROCHEMIE GMBH) * claims *	1	C06D5/06 C06B45/00
A	FR 2 234 246 A (SOCIETE NATIONALE DES POUDRES ET EXPLOSIFS) * claims *	1	
A	CHEMICAL ABSTRACTS, vol. 109, no. 22, 28 November 1988 Columbus, Ohio, US; abstract no. 193236g, K. KISHI ET AL.: "Gas generator for automobile air bag." page 174; XP000015814 * abstract * & JP 63 176 387 A (DAICEL CHEMICAL INDUSTRIES, LTD.)	1	
A	WO 95 00462 A (AUTOMOTIVE SYSTEMS LABORATORY, INC.) * page 1, line 23 - page 3, line 2 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP 0 659 715 A (MORTON INTERNATIONAL, INC.) * claims *	1-8	C06D C06B
D	& US 5 467 715 A (R.D. TAYLOR ET AL.)		
A	US 3 902 934 A (H.G. TIMMERMAN) * column 3, line 45 - line 61; claims *	1-8	
A	DE 43 18 883 A (TRW INC.) * column 14, line 13 - line 25; claims *	1	
A	DE 39 33 555 A (BAYERN-CHEMIE GESELLSCHAFT FÜR FLUGCHEMISCHE ANTRIEBE MBH) * column 2, line 25 - line 50; claims *	1	
	-/--		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 January 1997	Examiner Schut, R
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background U : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (01/96) (PC/CH)

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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 7233

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US 5 034 070 A (G.W. GOETZ ET AL.) * claims * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 January 1997	Examiner Schut, R
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>A : member of the same patent family, corresponding document</p>			

CPO FORM 1501 (04/94) (P04001)